

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 740 490 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
30.10.1996 *Bulletin* 1996/44

(51) Int. Cl.⁶: **H05B 33/14**, C09K 11/00,
C09K 11/62, C09K 11/64

(21) Application number: 95930023.7

(86) International application number:
PCT/JP95/01739

(22) Date of filing: 31.08.1995

(87) International publication number:
WO 96/15648 (23.05.1996 *Gazette* 1996/23)

(84) Designated Contracting States:
DE FR GB

(30) Priority: 14.11.1994 JP 302725/94

(71) Applicants:
• MITSUI MINING & SMELTING CO., LTD.
Tokyo (JP)
• SHARP KABUSHIKI KAISHA
Osaka-shi Osaka 545 (JP)

(72) Inventors:
• SUGIOKA, Akiko-Mitsui Min. & Smelting R & D
Cent.
Saitama 362 (JP)
• TAKAHASHI, Noriyuki-Mitsui Min. & Smelting
Corp.
Saitama 362 (JP)

• YASHIMA, Isamu-Mitsui Min. & Smelt. Corp. R&D
Cen.
Saitama 362 (JP)
• HIGUCHI, Makoto-Kamioka Min. & Smelting Co.
Ltd.
Yoshiki-gun-Gifu 506-11 (JP)
• MIKAMI, Akiyoshi-Sharp Kabushikikaisha
Osaka 545 (JP)
• TERADA, Kousuke-Sharp Kabushikikaisha
Osaka 545 (JP)
• OKADA, Katsuhiro-Sharp Kabushikikaisha
Osaka 545 (JP)

(74) Representative: Modiano, Guido, Dr.-Ing. et al
Modiano, Josif, Pisanty & Staub,
Baaderstrasse 3
80469 München (DE)

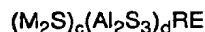
(54) **THIN-FILM ELECTROLUMINESCENT ELEMENT**

(57) A thin film electro-luminescence material comprising an alkaline earth metal thiogallate represented by the following compositional formula:

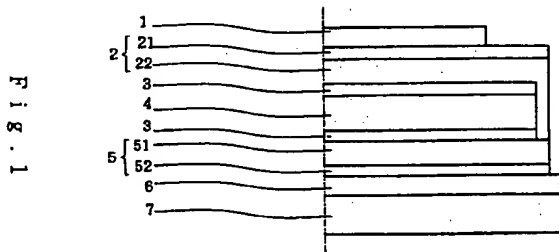


wherein M_1 is Sr or Ba; RE is a lanthanoid element; and a and b are integers which are different from each other

or comprising an alkaline earth metal thioaluminate represented by the following compositional formula:



wherein M_2 is Ca, Sr or Ba; RE is a lanthanoid element; and c and d are integers which may be identical with or different from each other,
and a thin film electro-luminescence device comprising said thin film electro-luminescence material as a luminescence layer.



EP 0 740 490 A1

Description

[Technical Field]

This invention relates to an electro-luminescence device (hereinafter abbreviated to "EL" device) luminescing by the application thereto of an electric field and more particularly to a thin film EL material useful in the thin film luminescence layer of the device and a thin film EL device using said material therein.

[Prior Art]

Studies of red color-, green color- and blue color-emitting EL materials are in progress to attain the full coloration of a thin film EL panel. However, there has not been obtained yet any satisfactory blue color-emitting material exhibiting high luminance and excellent chromatic purity (excitation purity). One of the most advanced blue color-emitting materials is SrS:Ce and has recently been developed to have remarkably improved luminance and chromatic purity. However, it is anticipated from, for example, the size of the site for Ce as a substituent that the luminescence peak of SrS:Ce is not shifted to the side of a wavelength shorter than about 480 nm and therefore SrS:Ce does not emit pure blue-colored light. Further, SrS itself exhibits deliquescence and requires heating at 1400°C or above and the like to be completely synthesized, thereby to constitute a barrier to the industrial production thereof.

A thin film EL device using $\text{M}\text{Ga}_2\text{S}_4\text{:Ce}$ therein (wherein M is an alkaline earth metal) has recently been developed and attracts attention since it exhibits high luminance and luminesces at a shorter wavelength (Japanese Pat. Appln. Laid-Open gazette No. Hei. 5-65478). Further, Davlous et al. reported that strontium thiogallate and barium thiogallate each having Eu^{2+} added thereto luminesce mainly in the blue-color region [J. Solid. State Chem. 83, 316 (1989)]. Additionally, LeThi et al. reported that alkaline earth metal thioaluminates each having Eu^{2+} added thereto luminesce mainly in the green-color region [Mat. Sci. Eng. B14 (1992) 393]. As compared with SrS, such thiogallates and thioaluminates have an advantage that their synthesis temperature is generally as low as about 1100°C, this being industrially superior. The thioaluminate corresponds to a compound prepared by replacing the gallium of the thiogallate by aluminum, and the site for a lanthanoid element as a substituent (in other words, the site for an alkaline earth metal) in the thioaluminate tends to be generally larger than that in the thiogallate. Accordingly, it is thought that the emission spectrum of the thioaluminate is shifted to a shorter wavelength side thereby to emit purer blue particularly when the thioaluminate contains Eu or Ce as a substituent.

However, there has not been obtained as yet any satisfactory blue-emitting thin film EL device which is more excellent in chromatic (excitation) purity and chromaticity coordinates.

[DISCLOSURE OF THE INVENTION]

An object of this invention is to provide a thin film EL material from which a blue-emitting body for EL is obtained and which is excellent in chromaticity coordinates and easily producible industrially production can be produced and also to provide a thin film EL device comprising a luminescence layer made from said material.

The above object can be attained by providing a thin film EL material which will now be described below.

More particularly, this invention resides in a thin film EL material comprising an alkaline earth metal thiogallate represented by the following compositional formula:



(wherein M_1 is Sr or Ba; RE is a lanthanoid element; and a and b are integers which are different from each other).

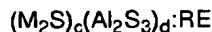
In the above formula, as described above, M_1 represents strontium (Sr) or barium (Ba); and RE represents a lanthanoid element such as lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd) or europium (Eu). Among these lanthanoid elements, cerium is preferably used and is inexpensive and therefore economical. Although a and b are each an integer, they are different from each other.

As described above, this invention resides in a thin film EL material comprising the above alkaline earth metal thiogallate as the matrix and an lanthanoid element such as cerium as the dopant (luminescence center). Examples of the composition of such a thin film electro-luminescence material are $\text{BaGa}_4\text{S}_7\text{:Ce}$, $\text{Ba}_3\text{Ga}_2\text{S}_6\text{:Ce}$ and $\text{Sr}_2\text{Ga}_2\text{S}_5\text{:Ce}$. Additionally, it is preferable that the thin film EL material of this invention further contain a charge compensation agent such as potassium.

Such a thin film EL material can be produced by, e.g., the following process. More particularly, it is produced by mixing SrCO_3 or BaCO_3 with Ga_2O_3 in a proper molar ratio, adding CeF_3 as a material for the dopant and KCL as a material for the charge compensation agent to the obtained mixture and then firing the whole thus obtained at 900 to 1100°C in a H_2S atmosphere. Of course, SrS, BaS, Ga_2S_3 , CeO_2 and the like may be used instead of the above raw materials

and material for the charge compensation agent is not limited to potassium but may be any compound which may give a monovalent cation having a proper ion radius. Alternatively, the charge compensation agent may be a trivalent anion having a proper ion radius.

This invention also resides in a thin film EL material characterized by being composed of an alkaline earth metal thioaluminate represented by the following compositional formula:



[wherein M_2 is Ca, Sr or Ba; RE is a lanthanoid element; and c and d are integers which may be identical with or different from each other].

In the above formula, as described above, M_2 represents calcium (Ca), strontium (Sr) or barium (Ba); and RE represents a lanthanoid element such as lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd) or europium (Eu), among which cerium or europium is preferably used. In particular, as described above, cerium is inexpensive and therefore economical. Further, c and d are each an integer and they may be identical with or different from each other.

As described above, this invention also resides in a thin film EL material comprising the above alkaline earth metal thioaluminate as the matrix material and a lanthanoid element such as cerium as the dopant (luminescence center). Examples of such a thin film EL material are $SrAl_2S_4$, $CaAl_2S_4$, $Ca_2Al_2S_5$, $BaAl_2S_4$, $BaAl_4S_7$, $Ba_4Al_2S_7$, $Ba_5Al_2S_8$, $Sr_2Al_2S_5$ and $Ba_2Al_2S_5$.

Such a thin film EL material can be produced by, e.g. the following process. Namely, it is produced by sulfureting $CaCO_3$, $SrCO_3$, $BaCO_3$, or the like under suitable conditions to obtain CaS, SrS, BaS or the like, mixing the alkaline earth metal sulfide with Al_2S_3 in a proper molar ratio, adding $CeCl_3$ or Eu_2O_3 as a dopant material to the resulting mixture and then firing the whole thus obtained at 900 to 1000°C in a H_2S atmosphere. Of course, Al_2O_3 , CeO_2 , CeF_3 , Ce_2F_3 , EuF_3 and the like may be used instead of the above compounds as starting materials. Alternatively, a mixture preliminarily prepared by mixing an alkaline earth metal compound with an aluminum compound may be sulfuretted at one time. Furthermore, when Ce is used as a dopant, the co-addition of a monovalent cation (such as K or Na) having a proper ion radius and a trivalent anion as charge compensation agents increases the resulting EL material in intensity of luminescence.

The thin film EL device of this invention is one comprising a luminescence layer made from the above thin film EL material. Fig. 1 shows an example of the constitution of such a thin film EL device. In Fig. 1, numeral 1 refers to an upper electrode (rear electrode) made of Al or the like, 2 (21 and 22) an upper insulating layer, 3 a buffer layer, 4 a luminescence layer, 5 (51 and 52) a lower insulating layer, 6 a lower electrode (transparent electrode) made of ITO ($In_2O_3-SnO_2$) and 7 a glass substrate.

The thin film EL device shown in Fig. 1 is a double-insulated one in which the luminescence layer is sandwiched in between the upper and lower insulating layers (films) and which has a structure produced by stacking one upon another a lower electrode (transparent electrode), a lower insulating layer, a buffer layer, a luminescence layer, a buffer layer, an upper insulating layer and an upper electrode (rear electrode) on a glass substrate in said order. An ITO film is used as the transparent electrode, which can be formed into a film having a thickness of about 20 nm by an electron beam (EB) vapor deposition or high frequency sputtering method. The lower insulating layer can be formed by making SiO_2 grow by a high frequency sputtering method and then making Si_3N_4 grow on the SiO_2 layer in a stacked state. Although the luminescence layer may be formed by an EB evaporation method, a high-frequency sputtering method or the like. In Example 4 which will be described later, the luminescence layer was formed by sputtering at a substrate temperature of 100 to 150°C in an Ar gas atmosphere containing 8% of hydrogen sulfide. A Si_3N_4 layer and a SiO_2 layer are formed by high-frequency sputtering as the upper insulating layer, followed by heat treatment to 630 to 700°C in a vacuum for about one hour to further form on said layer an upper electrode made of Al or the like by vacuum vapor deposition.

The upper insulating layer 2 is composed of a SiO_2 layer 21 and a Si_3N_4 layer 22, while the lower insulating layer 5 is composed of a Si_3N_4 layer 51 and a SiO_2 layer 52. The thicknesses of the foregoing layers are, e.g., as follows: SiO_2 layer 21, 0.005 μm ; Si_3N_4 layer 22, 0.12 μm ; buffer layer 3, 0.1 μm ; luminescence layer 4, 0.6 μm ; Si_3N_4 layer 51, 0.2 μm ; and SiO_2 layer 52, 0.05 μm .

[BRIEF DESCRIPTION OF THE DRAWINGS]

Fig. 1 is a schematic view showing the constitution of a thin film EL device of this invention;

Fig. 2 is a graph showing the photo-luminescence of $BaGa_4S_7:Ce,K$, a material for an EL device;

Fig. 3 is a graph showing the electro-luminescence of a $BaGa_4S_7:Ce, K$ thin film EL device;

Fig. 4 is a graph showing the photo-luminescence of $Ba_3Ga_2S_6:Ce,K$, a material for an EL device;

Fig. 5 is a graph showing the photo-luminescence of $Sr_2Ga_2S_5:Ce,K$, a material for an EL device;

Fig. 6 is a graph showing the electro-luminescence of a $Sr_2Ga_2S_5:Ce,K$ thin film EL device;

Fig. 7 is a chromaticity diagram showing the chromaticity coordinates of a $Sr_2Ga_2S_5:Ce,K$ thin film EL device, a $BaGa_4S_7:Ce,K$ thin film EL device and a $SrS:Ce$ thin film EL device;

Fig. 8 shows the emission spectra of thioaluminates according to this invention wherein M_2 is Ba (Ce and K added);
 Fig. 9 shows the emission spectra of thioaluminates according to this invention wherein M_2 is Ba (Eu added);
 Fig. 10 shows the emission spectra of a thin film EL device comprising a luminescence layer made of $BaAl_2S_4:Eu$;
 Fig. 11 shows the emission spectra of thioaluminates according to this invention wherein M_2 is Sr (Ce and K added);
 Fig. 12 shows the emission spectra of thioaluminates according to this invention wherein M_2 is Sr (Eu added);
 Fig. 13 shows the emission spectra of a thin film EL device comprising a luminescence layer made of $SrAl_2S_4:Eu$;
 Fig. 14 shows the emission spectrum of a thioaluminates according to this invention wherein M_2 is Ca (Ce and K added); and
 Fig. 15 shows the emission spectra of thioaluminates according to this invention wherein M_2 is Ca (Eu added).

[Example]

This invention will now be illustrated by referring to the following Examples.

Example 1

A mixture composed of $BaCO_3$ and Ga_2O_3 in a molar ratio of 1 : 2 was provided as a starting material, heated to $900^\circ C$ in a H_2S atmosphere for 5 hours and then screened to adjust particle sizes. The resulting material was heated to $1000^\circ C$ in a H_2S atmosphere for 5 hours, again screened to adjust particle sizes and then incorporated with CeF_3 and KCl each in an amount of 10 mol %. The mixture thus obtained was heated to $1100^\circ C$ in a H_2S atmosphere for 5 hours. The compound $(BaGa_4S_7:Ce,K)$ thus obtained was excited at 374 nm to present photo-luminescence which is shown in Fig. 2. It can be understood from Fig. 2 that the photo-luminescence has a peak in the neighborhood of 460 nm.

Further, a thin film luminescence layer made of the above compound and an insulating layer were formed under the conditions specified in Table 1, after which a thin film EL device as shown in Fig. 1 was produced. This device exhibited blue electro-luminescence which is indicated in Fig. 3. The chromaticity coordinates of the electro-luminescence are: $X = 0.153$ and $Y = 0.136$. The luminance was 0.7 cd/m^2 when the device was driven at 1 kHz.

Table 1

Film-forming conditions	Luminescence layer	Insulating layer (Si_3N_4)
method of growth	high-frequency magnetron sputtering method	
sputtering gas	H_2S (5%) + Ar (95%)	
pressure of gas (Pa)	2	0.8
substrate temp. ($^\circ C$)	100 ~ 300	250
sputtering electric power (W)	150	750
rate of growth (A/min)	50	100
target size (mm)	80 \varnothing	250 \varnothing

Example 2

A mixture composed of $BaCO_3$ and Ga_2O_3 in a molar ratio of 3 : 1 as a starting material was heated to $900^\circ C$ in a H_2S atmosphere for 5 hours. The mixture so heated was screened to adjust particle sizes. The resulting material was heated to $1000^\circ C$ in a H_2S atmosphere for 5 hours, again screened to adjust particle sizes, thereafter incorporated with CeF_3 and KCl in respective amounts of 1 mol % and 0.1 mol % and then further heated to $1100^\circ C$ in a H_2S atmosphere for 5 hours. The photo-luminescence of the thus obtained compound $(Ba_3Ga_2S_6:Ce,K)$ is shown in Fig. 4. It can be understood from Fig. 4 that the photo-luminescence has a peak in the neighborhood of 470 nm.

Example 3

A mixture composed of SrCO_3 and Ga_2O_3 in a molar ratio of 2 : 1 as a starting material was heated to 880°C in a H_2S atmosphere for 5 hours and then adjusted in particle sizes by screening. The resulting material was heated to 880°C in a H_2S atmosphere for 5 hours, thereafter again screened to adjust particle sizes, incorporated with CeF_3 and KCl each in an amount of 10 mol % and then further heated to 880°C in a H_2S atmosphere for 5 hours. The photo-luminescence of the thus obtained compound ($\text{Sr}_2\text{Ga}_2\text{S}_5:\text{Ce,K}$) is shown in Fig. 5, from which it can be understood that the photo-luminescence has a peak in the neighborhood of 460 nm.

A thin film luminescence layer made of the above compound and an insulating layer were formed under the conditions specified in Table 1, and, further, a thin film EL device as shown in Fig. 1 was produced. This device exhibited blue electro-luminescence, which is shown in Fig. 6. The chromaticity coordinates of the electro-luminescence are: $X = 0.22$ and $Y = 0.346$. The luminance was 2.4 cd/m^2 when the device was driven at 1 kHz.

Fig. 7 shows the chromaticity coordinates ($X = 0.153$, $Y = 0.136$) of the $\text{BaGa}_4\text{S}_7:\text{Ce,K}$ thin film EL device produced in Example 1, those ($X = 0.22$, $Y = 0.346$) of the $\text{Sr}_2\text{Ga}_2\text{S}_5:\text{Ce,K}$ thin film EL device produced in Example 3 and those ($X = 0.18$, $Y = 0.38$) of a $\text{SrS}:\text{Ce}$ thin film EL device for reference.

Example 4

BaCO_3 as a starting material was heated in a H_2S atmosphere to 500°C for 2 hours, to 600°C for 2 hours and then to 900°C for 4 hours, followed by screening to adjust particle sizes. The resulting material was heated to 1000°C in a H_2S atmosphere for 4 hours, followed by screening to again adjust particle sizes thus obtaining BaS . The BaS thus obtained was mixed with Al_2S_3 , CeCl_3 , KCl and Eu_2O_3 in molar ratios specified in Table 2 and then the obtained mixtures were each heated to 1000°C in a H_2S atmosphere for 5 hours.

Table 2

	molar ratio		mol %		
	BaS	Al_2S_3	CeCl_3	KCl	Eu_2O_3
$\text{BaAl}_2\text{S}_4:\text{Ce,K}$	1	1	1	1	0
$\text{BaAl}_2\text{S}_4:\text{Eu}$	1	1	0	0	1
$\text{BaAl}_4\text{S}_7:\text{Ce,K}$	1	2	1	1	0
$\text{BaAl}_4\text{S}_7:\text{Eu}$	1	2	0	0	1
$\text{Ba}_2\text{Al}_2\text{S}_5:\text{Ce,K}$	2	1	1	1	0
$\text{Ba}_2\text{Al}_2\text{S}_5:\text{Eu}$	2	1	0	0	1
$\text{Ba}_4\text{Al}_2\text{S}_7:\text{Eu}$	4	1	0	0	1
$\text{Ba}_5\text{Al}_2\text{S}_8:\text{Eu}$	5	1	0	0	1

The obtained compounds ($\text{BaAl}_2\text{S}_4:\text{Ce,K}$, $\text{BaAl}_4\text{S}_7:\text{Ce,K}$, $\text{Ba}_2\text{Al}_2\text{S}_5:\text{Ce,K}$, $\text{BaAl}_2\text{S}_4:\text{Eu}$, $\text{BaAl}_4\text{S}_7:\text{Eu}$, $\text{Ba}_2\text{Al}_2\text{S}_5:\text{Eu}$, $\text{Ba}_4\text{Al}_2\text{S}_7:\text{Eu}$ and $\text{Ba}_5\text{Al}_2\text{S}_8:\text{Eu}$) were excited at a proper wavelength between 280 and 350 nm and the emission spectra observed in this case are given in Figs. 8 and 9. It can be understood from Figs. 8 and 9 that the spectra have their respective peaks mainly in the blue region. Further, it can be understood therefrom that the full width at half maximum of the emission spectrum of the Eu-containing material is smaller than the Ce-containing material and is as small as about one-half of that of the Ce-containing material.

A thin film luminescence layer made of the $\text{BaAl}_2\text{S}_4:\text{Eu}$ prepared above and an insulating layer were formed under the conditions specified in Table 3, and then a thin film EL device as shown in Fig. 1 was produced.

Table 3

Film-forming conditions	Luminescence layer	Insulating layer (Si_3N_4)
method of growth	high-frequency magnetron sputtering method	
sputtering gas	$92\%\text{Ar} + 8\%\text{H}_2\text{S}$	Ar
pressure of gas (Pa)	2	0.8
substrate temp. ($^{\circ}\text{C}$)	100~150	200
sputtering electric power (W)	150	150
rate of growth (Å/min)	17~25	10
target size (mm)	80	250

The obtained thin film EL device exhibited blue electro-luminescence and the emission spectra of the device are given in Fig. 10. The chromaticity coordinates of the electro-luminescence are: $X = 0.283$ and $Y = 0.515$. The luminance was about 1 cd/m^2 when the device was driven at 1 kHz.

Example 5

SrS was mixed with Al_2S_3 while CeCl_3 , KCl and Eu_2O_3 were also mixed, in respective molar ratios specified in Table 4, after which the obtained mixtures were each heated to 1000°C in a H_2S atmosphere for 5 hours thereby to obtain compounds ($\text{SrAl}_2\text{S}_4\text{:Ce,K}$, $\text{Sr}_2\text{Al}_2\text{S}_5\text{:Ce,K}$, $\text{SrAl}_2\text{S}_4\text{:Eu}$ and $\text{Sr}_2\text{Al}_2\text{S}_5\text{:Eu}$). The compounds so obtained were excited at a proper wavelength from 280 to 350 nm and the emission spectra observed in this case are given in Figs. 11 and 12.

Table 4

	molar ratio		mol %		
	SrS	Al_2S_3	CeCl_3	KCl	Eu_2O_3
$\text{SrAl}_2\text{S}_4\text{:Ce,K}$	1	1	1	1	0
$\text{SrAl}_2\text{S}_4\text{:Eu}$	1	1	0	0	1
$\text{SrAl}_4\text{S}_7\text{:Ce,K}$	1	2	1	1	0
$\text{SrAl}_4\text{S}_7\text{:Eu}$	1	2	0	0	1

A thin film luminescence layer made of the $\text{SrAl}_2\text{S}_4\text{:Eu}$ prepared above and an insulating layer were formed under the conditions specified in Table 3, and then a thin film EL device as shown in Fig. 1 was produced. This thin film EL device exhibited blue electro-luminescence and the emission spectra of the thin film EL device are given in Fig. 13. The chromaticity coordinates of the electro-luminescence are: $X = 0.13$ and $Y = 0.377$. The luminance was about 1 cd/m^2 when the EL device was driven at 1 kHz.

Example 6

CaS was mixed with Al_2S_3 and, on the other hand, CeCl_3 , KCl and Eu_2O_3 are mixed together, in respective molar ratios specified in Table 5, after which the thus obtained mixtures were each heated to 1000°C in a H_2S atmosphere for 5 hours. Then the thus-obtained compounds ($\text{CaAl}_2\text{S}_4\text{:Ce,K}$, $\text{CaAl}_2\text{S}_4\text{:Eu}$ and $\text{Ca}_2\text{Al}_2\text{S}_5\text{:Eu}$) were excited at a proper wavelength between 280 and 350 nm and the emission spectra observed in this case are given in Figs. 14 and 15.

Table 5

	molar ratio		mol %		
	CaS	Al ₂ S ₃	CeCl ₃	KCl	Eu ₂ O ₃
CaAl ₂ S ₄ :Ce,K	1	1	1	1	0
CaAl ₂ S ₄ :Eu	1	1	0	0	1
Ca ₂ Al ₂ S ₅ :Eu	2	1	0	0	1

[Industrial Applicability]

It has been confirmed in this invention that the emission peaks of BaAl₂S₄:Ce,K, BaAl₄S₇:Ce,K, Ba₂Al₂S₅:Ce,K and so on appear in the neighborhood of 430 nm. The wavelengths of emission peaks thereof are shorter than those (480 nm) of SrS:Ce and those (460 nm) of MGa₂S₄:Ce (wherein M is an alkaline earth metal) by as much as 50 to 30 nm. Further, it has been ascertained that the Eu-containing material exhibits a full width at half maximum of as small as about one-half of that of the Ce-containing material thereby improving the former material in chromatic purity.

As described above, this invention makes it possible to obtain a thin film EL material excellent in chromaticity coordinates and chromatic purity, and a thin film EL device comprising said material as the luminescence layer.

Claims

1. A thin film electro-luminescence material comprising an alkaline earth metal thiogallate represented by the following compositional formula:



wherein M₁ is Sr or Ba; RE is a lanthanoid element; and a and b are integers which are different from each other.

2. A thin film electro-luminescence material comprising an alkaline earth metal thiogallate represented by the following compositional formula:



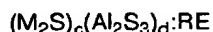
3. A thin film electro-luminescence material comprising an alkaline earth metal thiogallate represented by the following compositional formula:



4. A thin film electro-luminescence material comprising an alkaline earth metal thiogallate represented by the following compositional formula:



5. A thin film electro-luminescence material comprising an alkaline earth metal thioaluminate represented by the following compositional formula:



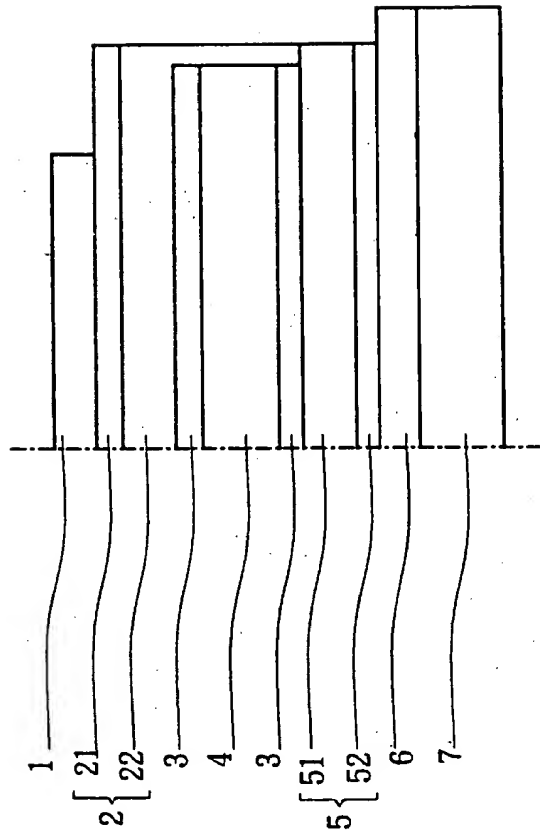
wherein M₂ is Ca, Sr or Ba; RE is a lanthanoid element; and c and d are integers which may be identical with or different from each other.

6. A thin film electro-luminescence material according to claim 5, wherein the alkaline earth metal thioaluminate is a member selected from the group consisting of SrAl₂S₄:Ce, CaAl₂S₄:Ce, BaAl₂S₄:Ce, BaAl₄S₇:Ce, Sr₂Al₂S₅:Ce,

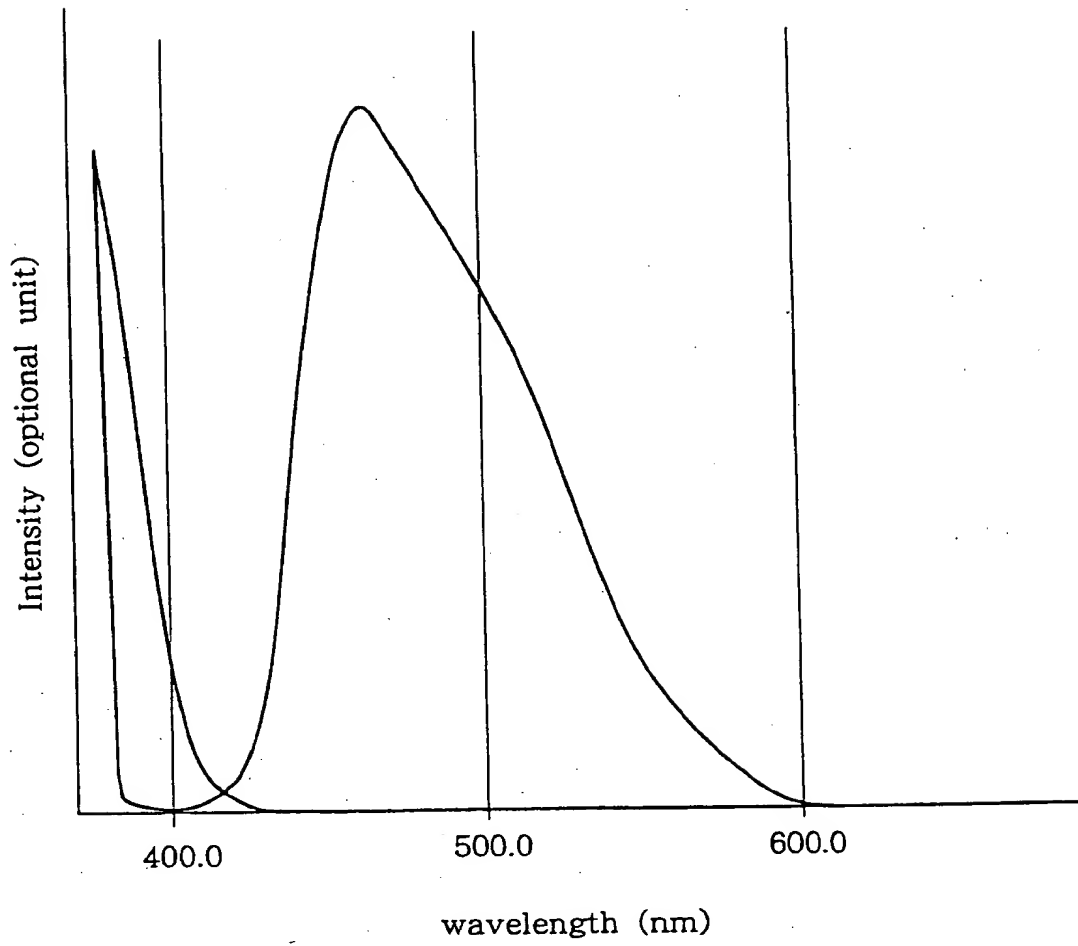
EP 0 740 490 A1

$\text{Ba}_2\text{Al}_2\text{S}_5:\text{Ce}$, $\text{SrAl}_2\text{S}_4:\text{Eu}$, $\text{BaAl}_2\text{S}_4:\text{Eu}$, $\text{BaAl}_4\text{S}_7:\text{Eu}$, $\text{Sr}_2\text{Al}_2\text{S}_5:\text{Eu}$, $\text{Ba}_2\text{Al}_2\text{S}_5:\text{Eu}$, $\text{CaAl}_2\text{S}_4:\text{Eu}$, $\text{Ca}_2\text{Al}_2\text{S}_5:\text{Eu}$, $\text{Ba}_2\text{Al}_2\text{S}_5:\text{Eu}$ and $\text{Ba}_5\text{Al}_2\text{S}_8:\text{Eu}$.

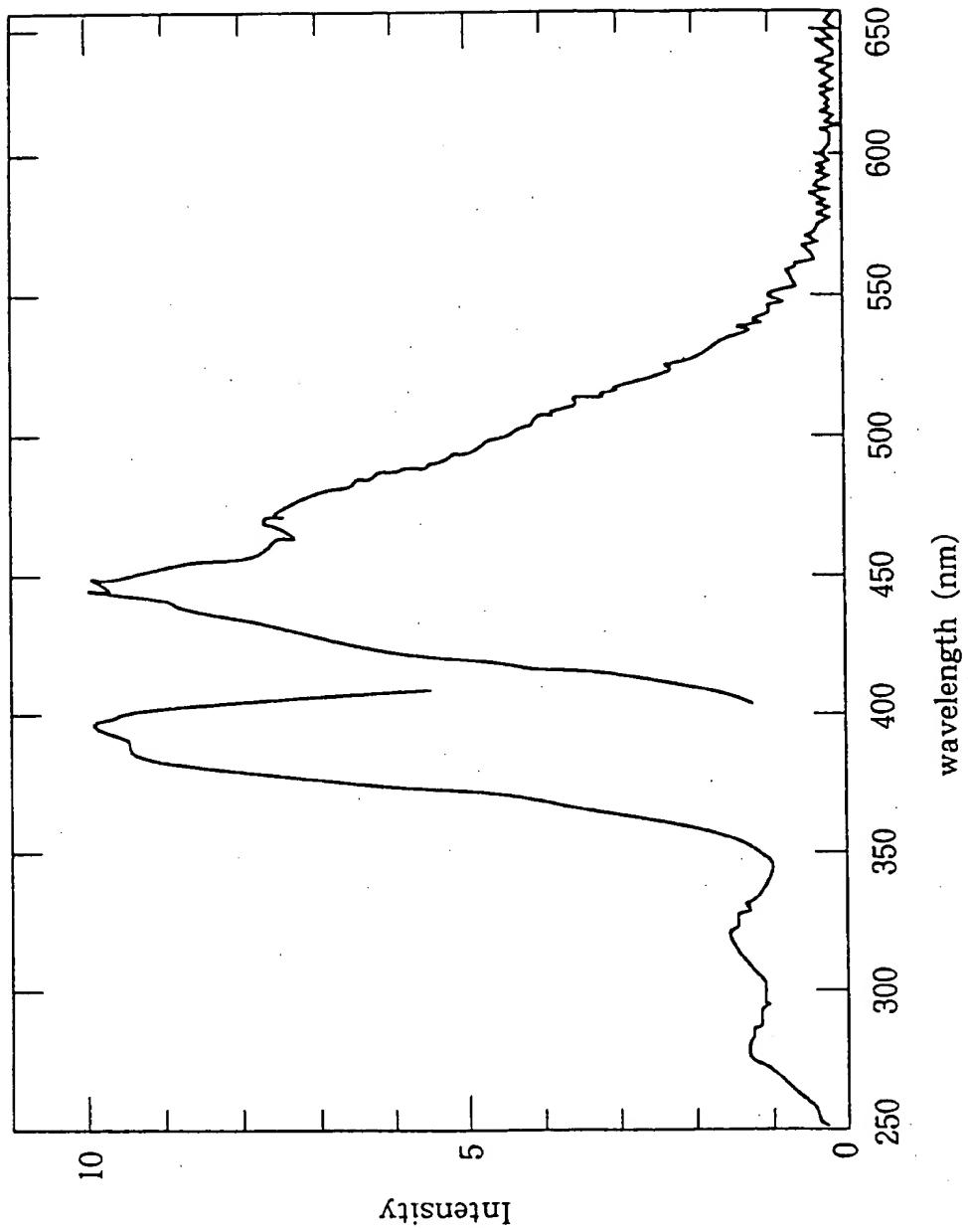
7. A thin film electro-luminescence device comprising any one of thin film electro-luminescence materials of claims 1 to 6 as a luminescence layer.



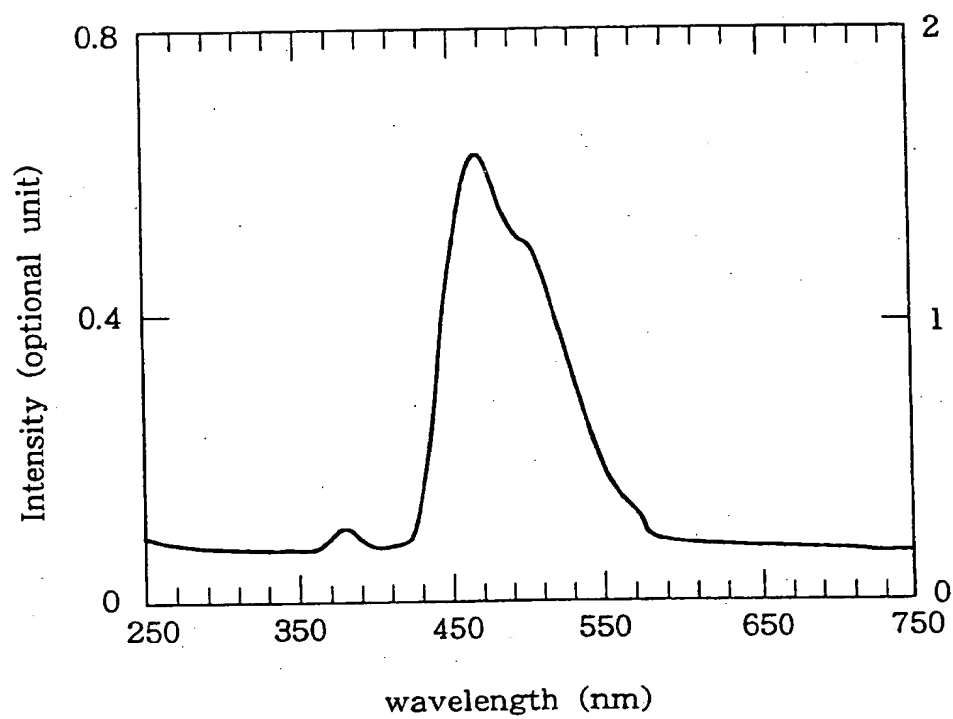
F i g . 1



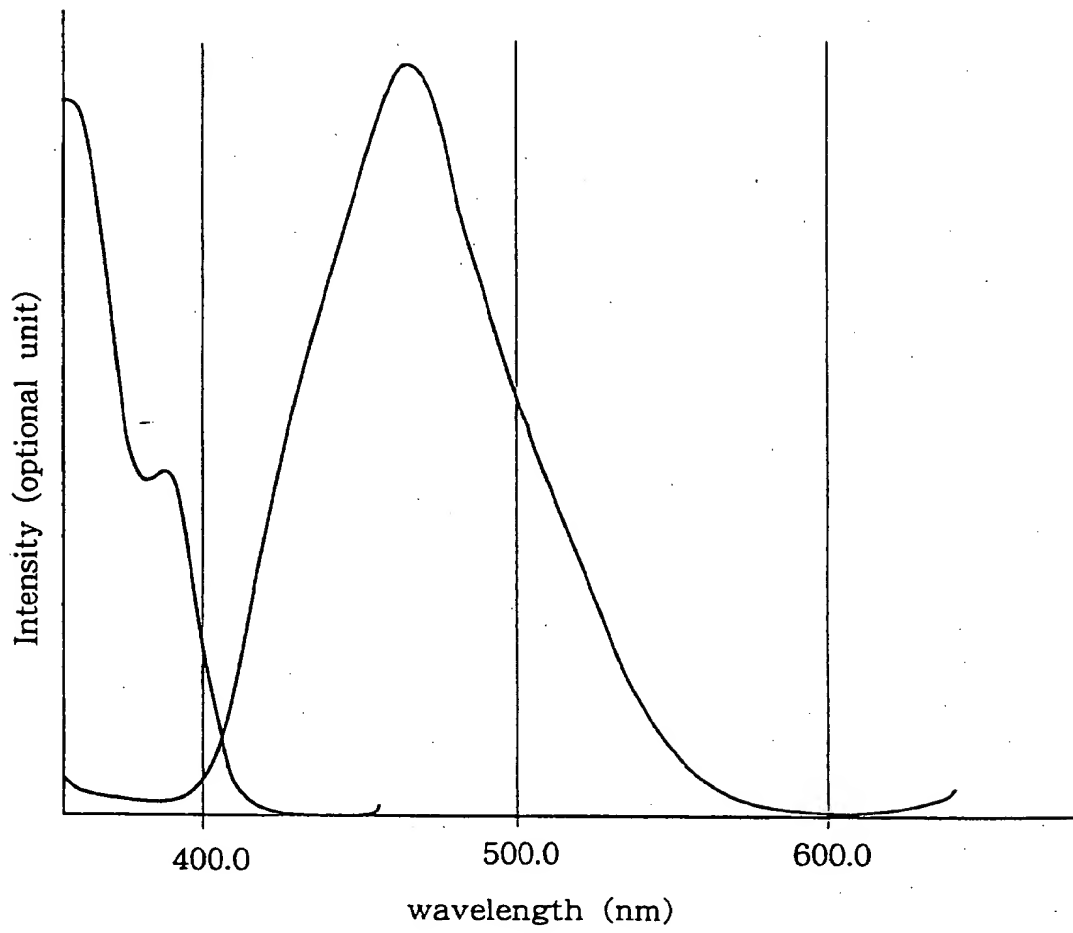
F i g . 2



F i g . 3



F i g . 4



F i g . 5

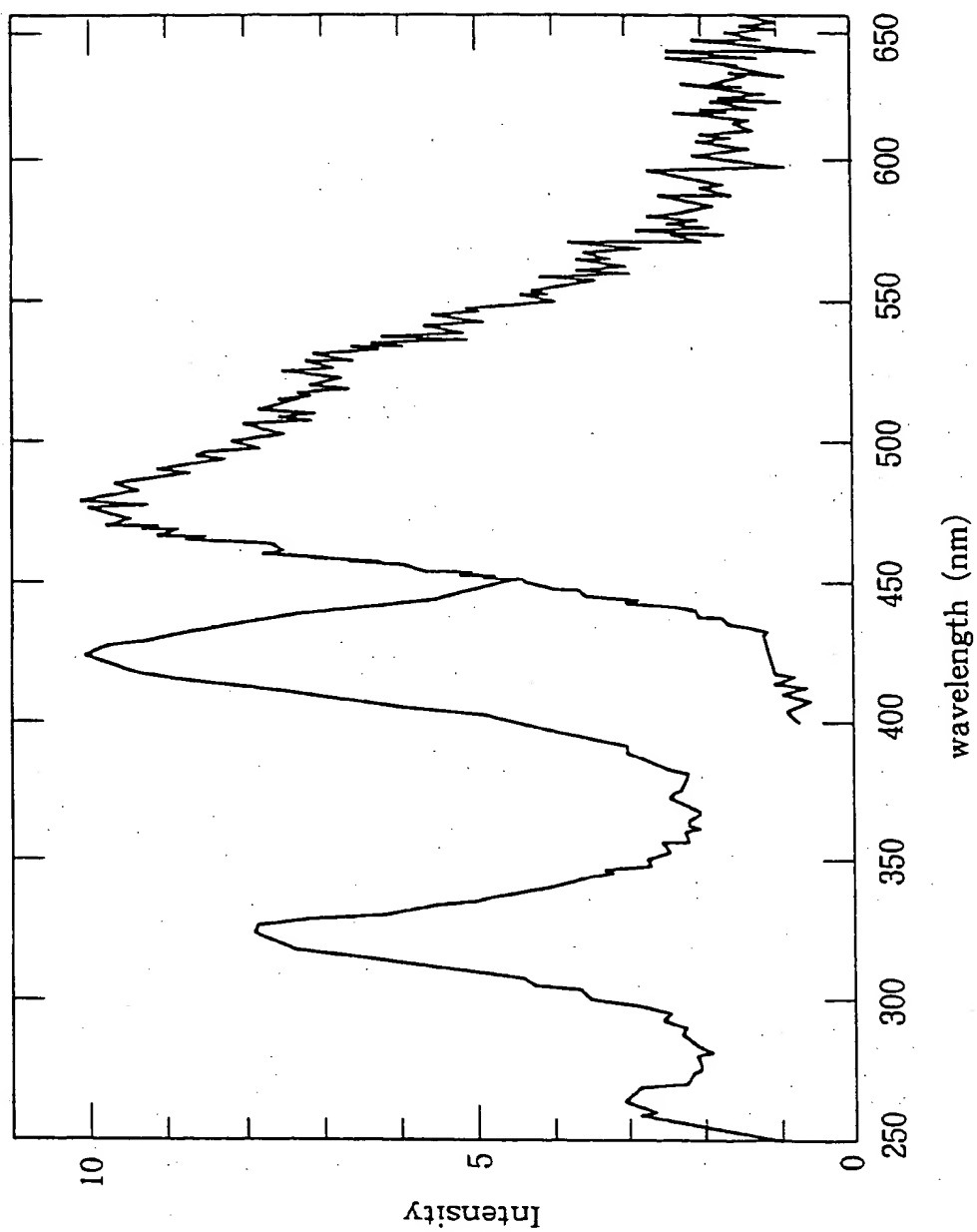


Fig. 6

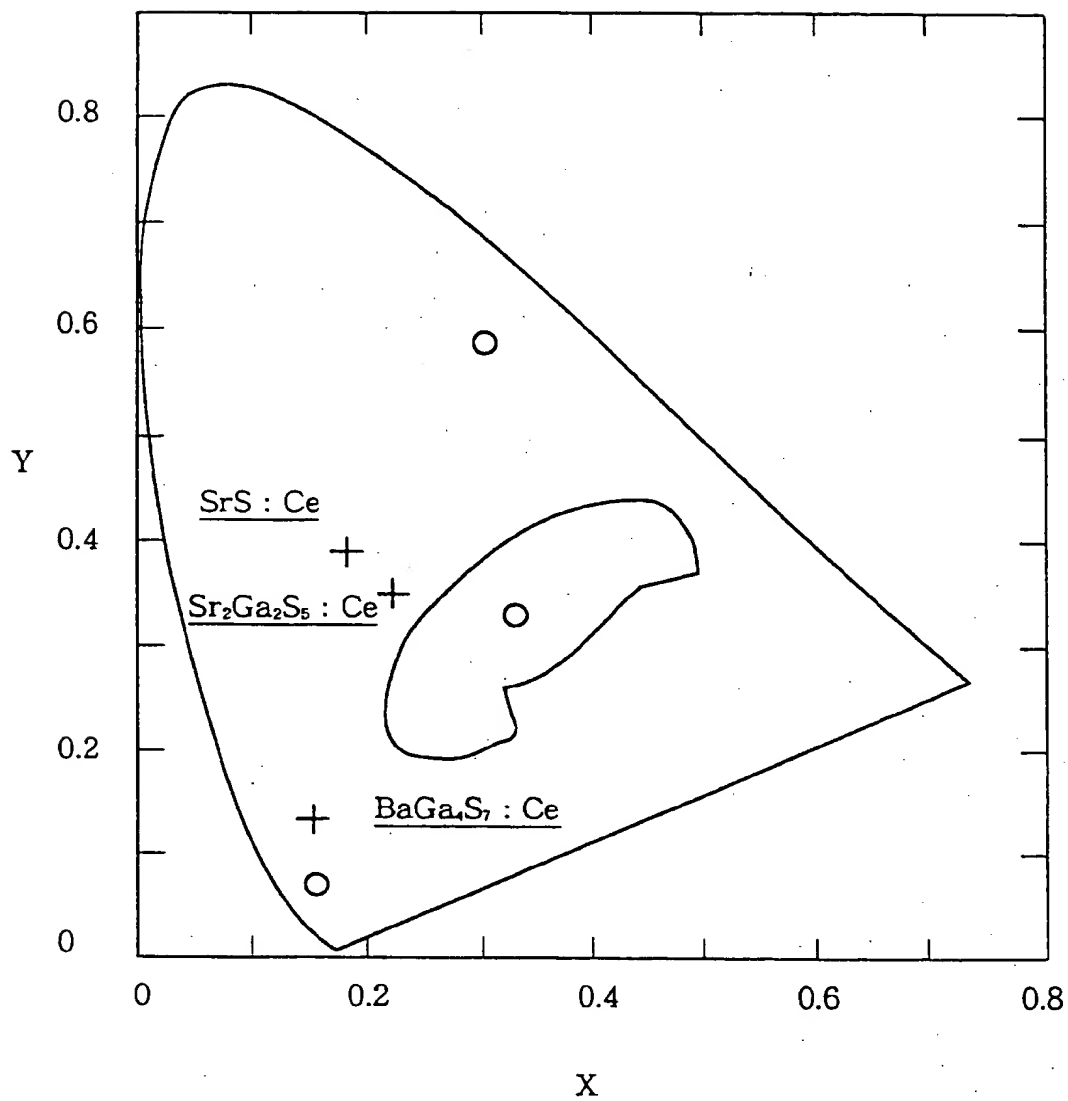
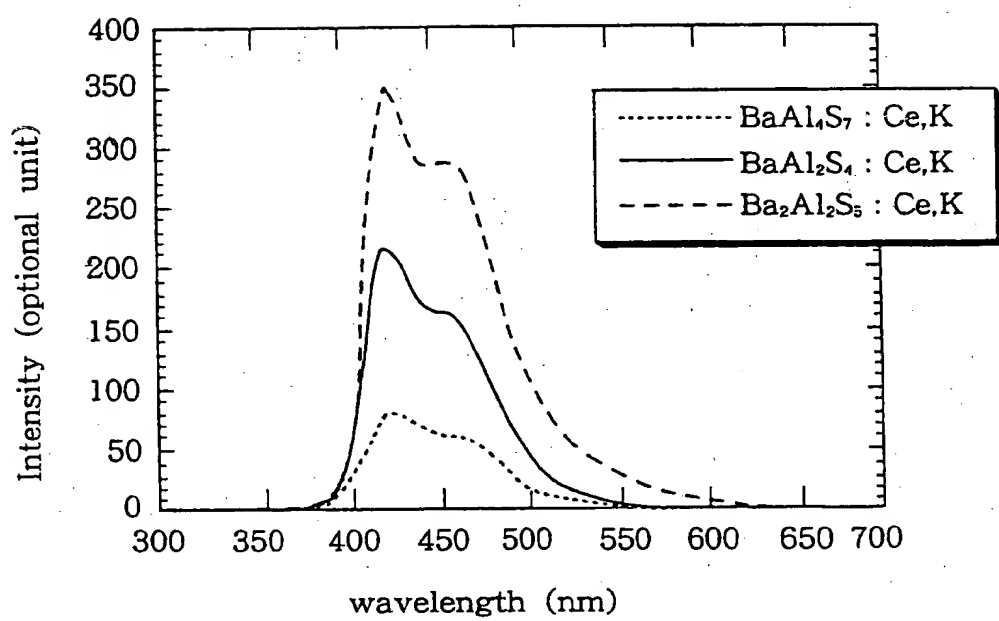
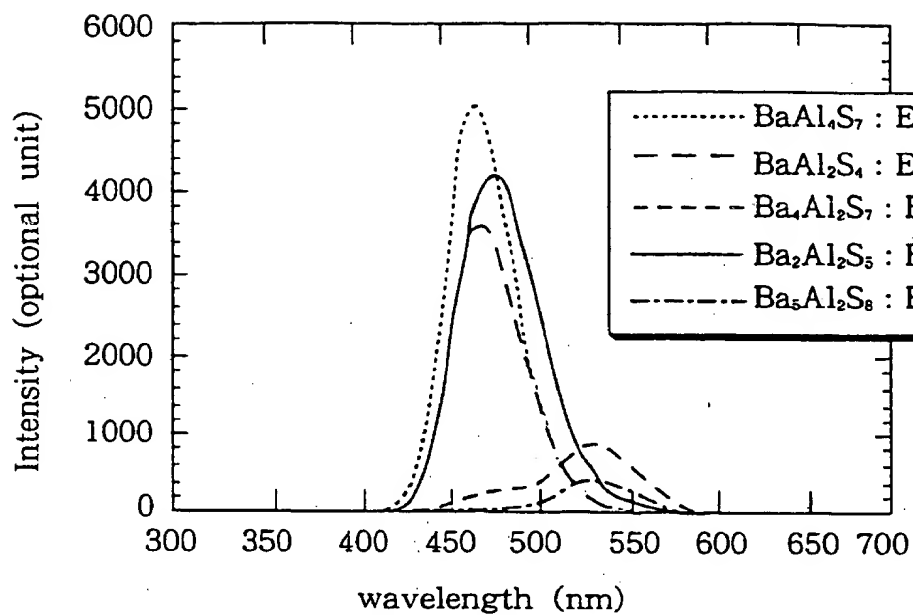


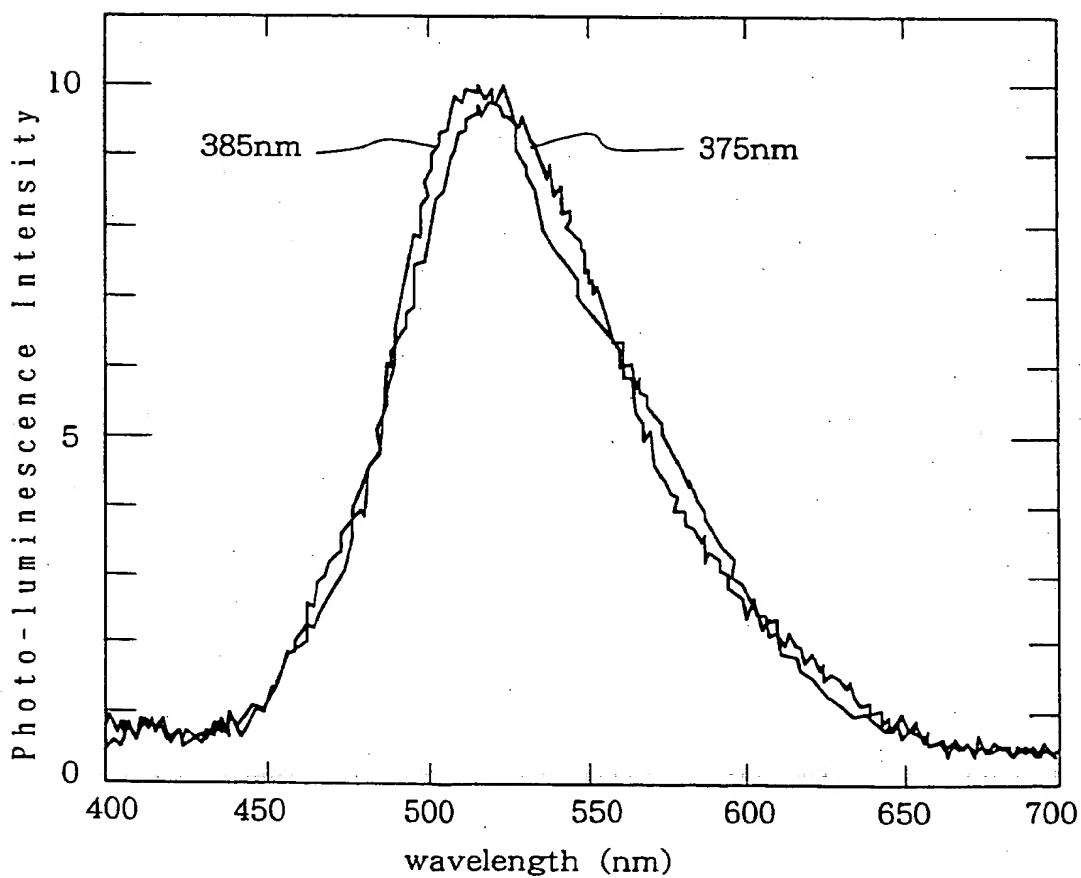
Fig. 7



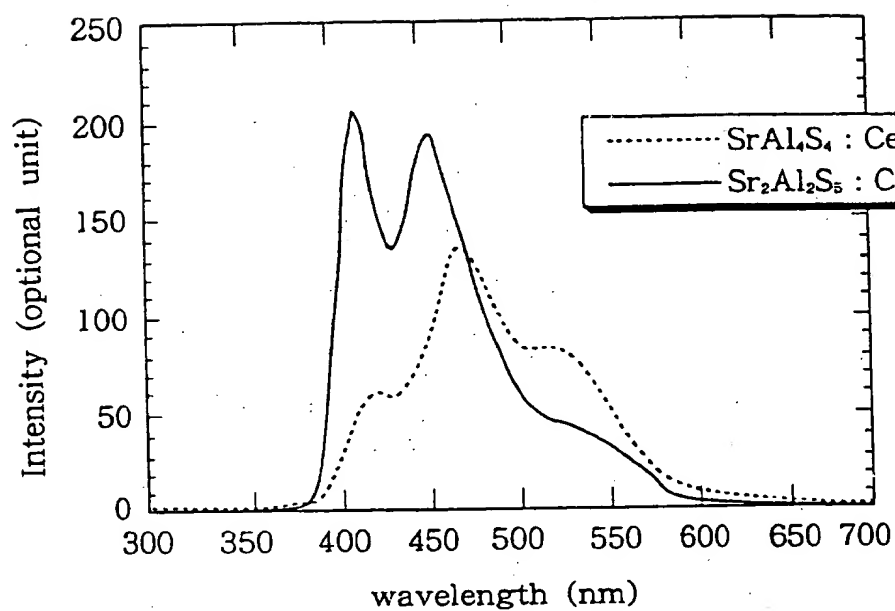
F i g . 8



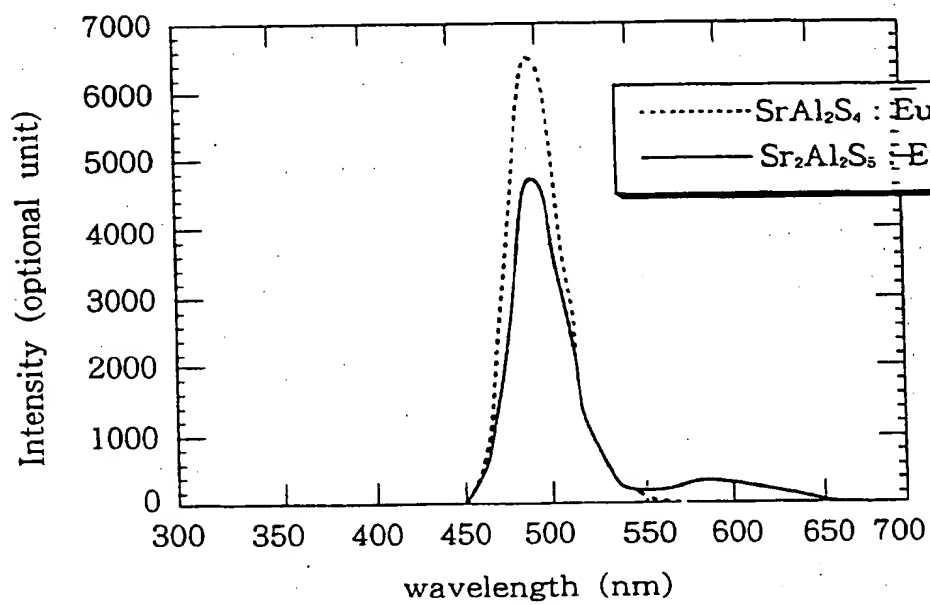
F i g . 9



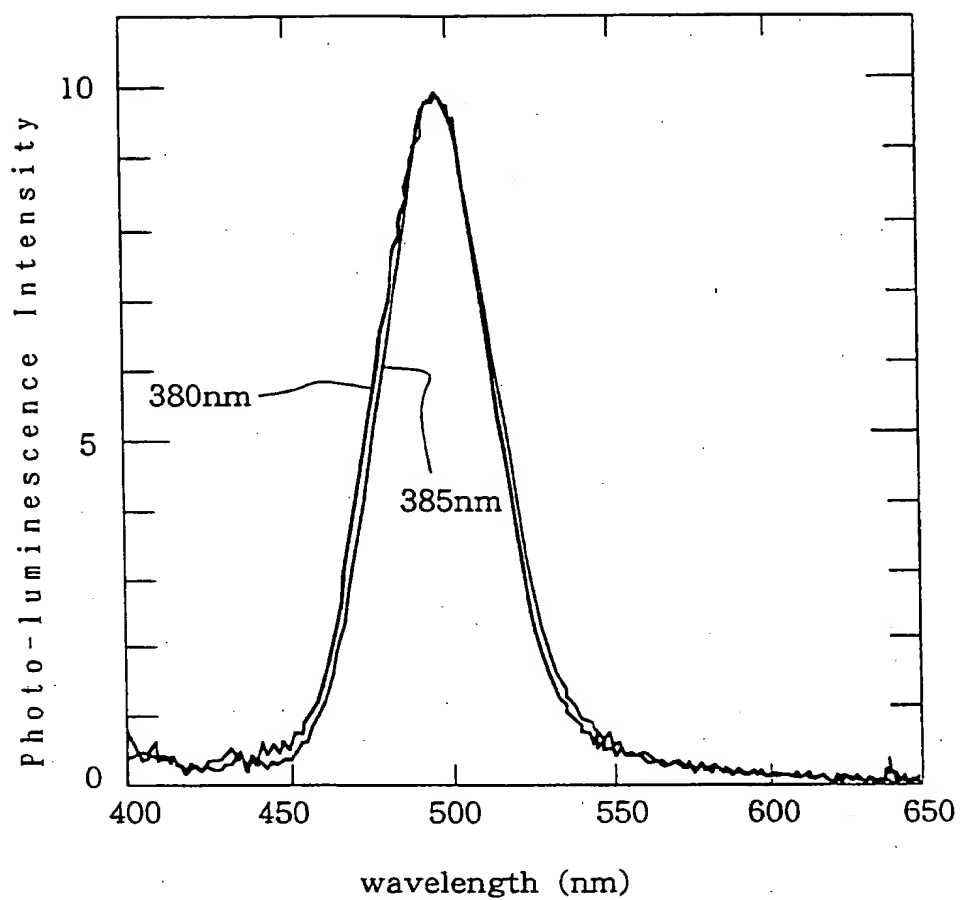
F i g . 1 0



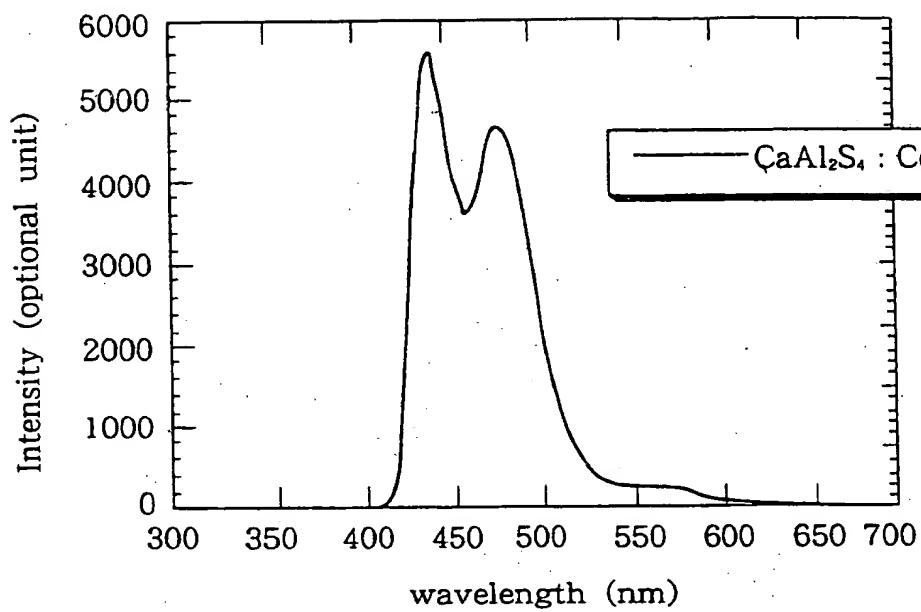
F i g . 1 1



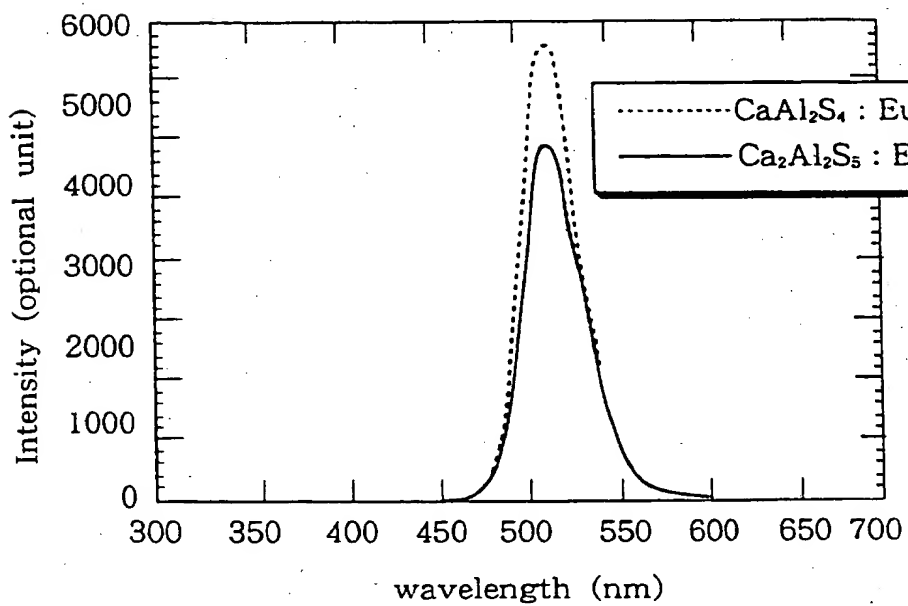
F i g . 1 2



F i g . 1 3



F i g . 1 4



F i g . 1 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP95/01.739

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl ⁶ H05B33/14, C09K11/00, C09K11/62, C09K11/64 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int. Cl ⁶ H05B33/14, C09K11/00, C09K11/62, C09K11/64 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926 - 1995 Kokai Jitsuyo Shinan Koho 1971 - 1995 Toroku Jitsuyo Shinan Koho 1994 - 1995 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
EX	JP, 7-242869, A (Mitsui Mining & Smelting Co., Ltd.), September 19, 1995 (19. 09. 95), Lines 1 to 20, column 1, Fig. 1 (Family: none)	1-4, 7
A	JP, 5-65478, A (Prenner Systems Inc.), March 19, 1993 (19. 03. 93), Lines 1 to 24, column 1, Fig. 1 & US, 5309070, A	1-4, 7
A	JP, 4-121992, A (Asahi Chemical Industry Co., Ltd.), April 22, 1992 (22. 04. 92), Lines 5 to 15, lower left column, page 1 (Family: none)	1-4, 7
A	JP, 63-218194, A (Sharp Corp.), September 12, 1988 (12. 09. 88), Lines 5 to 11, lower left column, page 1 (Family: none)	1, 5
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search November 13, 1995 (13. 11. 95)		Date of mailing of the international search report December 5, 1995 (05. 12. 95)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)